Unexpected contraction of a zeolite framework upon isomorphous substitution of Si by Al

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Isomorphous substitution of Si by Al in the framework of sodalites synthesized in ethylene glycol causes an unexpected contraction of the zeolite framework.

Isomorphous substitution of Si by other atoms in the framework of zeolites is an important area of investigation, because introduction of heteroatoms in a pure silica framework can convert essentially inactive materials into catalysts with potentially important applications. Catalytic activity can result from the introduction of a net negative charge in the framework when heteroatoms with a formal oxidation state of +3 (*e.g.* Al) substitute for Si.[1] In other cases, like in the important Ti-containing zeolites, the heteroatom by itself is responsible for the activity.[2]

The question of proving whether the intended isomorphous substitution has actually taken place is frequently difficult because single-crystal diffraction techniques to fully resolve a zeolite structure are limited by the microcrystalline nature of most zeolite samples. Other techniques (NMR, EPR, Rietveld refinement, XANES and EXAFS) can also present limitations related to the nature of the heteroatom or to its small concentration in the zeolite. Thus, the simple comparison of the unit-cell parameters of the unsubstituted and substituted materials is most frequently used to ascertain the isomorphous substitution: substitution of Si by a heteroatom T with a longer (shorter) bond distance to O should cause an increase (decrease) in the unit-cell volume of the material. A linear correlation (with the expected positive or negative slope) between the unit-cell volume and the heteroatom content (degree of substitution) is generally considered as sufficient proof of the isomorphous substitution in zeolites.[3]

However, this kind of proof of isomorphous substitutions in zeolites does not take into account the zeolite framework flexibility. Actually, the unit-cell size should not depend solely on the T–O bond distances, but also on the T–O–T angles, which can be influenced by a number of factors such as the nature, size and electric charge of the organic or inorganic matter present in the intrazeolitic voids. We present here recent results showing that isomorphous substitution of Si by Al can actually yield the opposite trend to the expected unit-cell expansion.

Four sodalite samples with Al/(Al + Si) molar ratios of 0, 0.043, 0.085 and 0.154 were synthesized by a method derived from that previously reported for pure silica sodalite.[4] Typically, NaOH (98%, EM) was disolved in ethylene glycol (Mallinkrodt) and then sodium aluminate ($Na_2O : Al_2O_3 : 3H_2O$, VWR) was added if required. Finally, amorphous silica (Cab-O-sil M-5) was added and the mixture stirred for one day at room temperature. Crystallization was allowed to proceed in Teflon lined 24 ml Parr bombs at 175 °C for three weeks. The samples were found by chemical analysis to contain Al and Si in the molar ratios given above, with Na^+ as counter cations and ethylene glycol molecules (two per unit cell) occluded in the intrazeolitic void space.

All the samples were phase pure and show very good crystallinities as seen by powder X-ray diffraction (XRD) using a Scintag XDS-2000 diffractometer (Cu-Kα radiation). The unit-cell size was determined by indexing the diffractograms recorded with fluorophlogopite as an internal standard (experimental conditions: step mode, 0.02° step size with 23 s per step, 2θ range 7–50°). No deviations from the cubic symmetry were observed in the range studied and systematic absences were consistent with a body-centred lattice. The unit-cell parameters were then refined using a least-squares procedure.

The isomorphous substitution of Al for Si in the sodalite framework was ascertained using spectroscopic techniques: the ^{27}Al MAS NMR spectra show only tetrahedral Al (δ 50–55, typical of Al in zeolites); the ^{29}Si MAS NMR spectra exhibit Si(nAl) resonances with $n = 0$ for pure silica, $n = 0$ and 1 for Si/Al ≈ 20, $n = 0$, 1 and 2 for Si/Al ≈ 10 and $n = 0$, 1, 2 and 3 for Si/Al ≈ 5 (n = no. of Als connected through O bridges to Si); from the intensities of these resonances Si/Al molar ratios of ∞, 17.8, 9.7 and 4.7 were calculated; and, finally, a linear correlation between the wavenumber of the infrared T–O asymmetric stretching vibration and the Al content was found (Fig. 1).

Although the isomorphous substitution is reasonably demonstrated we found the unexpected trend depicted in Fig. 2 between the cubic unit-cell edge and the Al content. Despite the long Al–O distance (1.70–1.78 Å) compared to the Si–O distance (1.57–1.67 Å), the unit cell of the sodalites synthesized in ethylene glycol undergoes a contraction as the Al content increases. This contraction is linear up to Al/(Al + Si) molar ratios of 0.085. The sample with Al/(Al + Si) = 0.154 slightly deviates from the linear trend. However, it still shows a unit-cell size smaller than the pure silica sample and is much smaller than expected. To illustrate this point, also plotted in Fig. 2 is the theoretical unit-cell expansion of sodalite as the degree of Al incorporation increases (assuming no changes in T–O–T angles) together with the value determined for a sodalite containing tetramethylammonium (TMA) with an Si/Al ratio of 5.[5] From Fig. 2 we infer that while pure silica and TMA-containing aluminosilicate sodalites have similar average

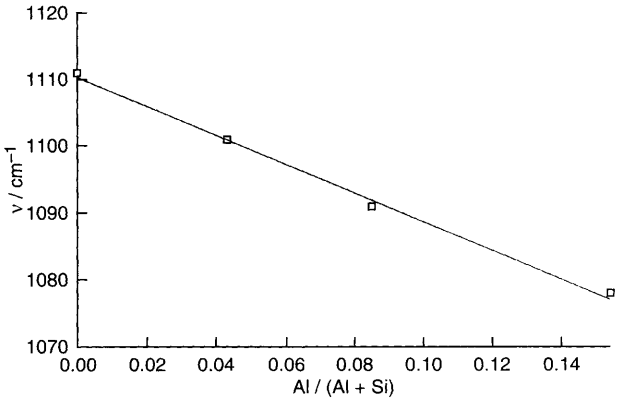

Fig. 1 Variation in position of the infrared T–O asymmetric vibration band with the Al content of sodalites

T–O–T angles (see below), the incorporation of aluminium in the samples synthesized in ethylene glycol media causes a decrease in T–O–T angles leading to a unit-cell contraction.

SOD has a very flexible zeolite topology as deduced from the very large range of T–O–T angles found in different materials having this topology (from 125 to 160°).[6] It has been shown that when the angle is 160° the O atoms lie at the faces of the [$4^6 6^8$] polyhedra (the 'sodalite cage') and the unit cell has the maximum possible size.[7] Those materials are said to have the 'fully expanded' sodalite framework. Rotation of the TO_4 tetrahedra can move the O atoms out of the polyhedral faces while maintaining the framework connectivity and the body-centred type of lattice (the space group changing from $Im\bar{3}m$ to $I\bar{4}3m$ if no distinction between Al and Si is made). This causes a unit-cell contraction with a reduction in T–O–T angles, and it is referred to as a 'partial collapse' of the framework. It is known that pure silica sodalite and the Na^+-free tetramethylammonium-containing sodalite are very near the fully expanded situation, with T–O–T angles of 159.7[8] and 157.8°,[5] respectively. From the chemical shift of the Si(0Al) NMR resonance we have calculated average T–O–T angles of 159.0, 156.2, 154.3 and 152.4° for Al/(Al + Si) ratios of 0, 0.043, 0.085 and 0.154, respectively, by using the equation developed by Thomas *et al.*[9] Thus, the observed contraction of the unit cell is accompanied by a decrease in the average T–O–T angle. In our opinion this is a consequence of the presence of increasing amounts of dehydrated Na ions as the Al content increases. These dehydrated cations with a relatively high polarizing power can displace the O atoms out of the [$4^6 6^8$] faces. The fact that in our samples Na^+ cations are dehydrated was deduced from thermogravimetric analyses and from ^1H MAS NMR spectroscopy [only for Al/(Al + Si) = 0.154 was a small water content found].[10] Similarly, when considering alkali–halide aluminosilicate sodalites with Si/Al ratios of 1 crystallized in aqueous media, the unit-cell edge has been shown to depend on the size (and hence the polarizing power) of the dehydrated alkali-metal cations inside the sodalite cage. These materials are generally far from the fully expanded situation (calculated a = 9.317 Å)[7] and a further contraction is found in the chloride sodalite series changing the cation from K^+ (a = 9.253 Å) to Na^+ (a = 8.879 Å) to Li^+ (a = 8.447 Å).[11]

Finally, SOD can be considered as lying right in the boundary region between zeolites and clathrasils and thus issues involving its physicochemical properties may not necessarily translate to other more open zeolites. However, the results shown here clearly demonstrate that one must use caution when interpreting substitution by means of lattice parameters alone.

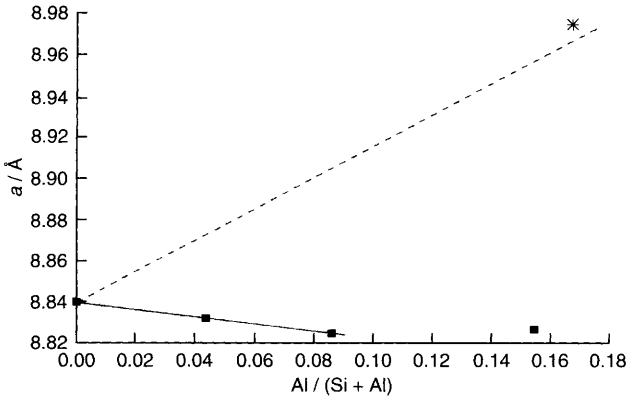

Fig. 2 Unit-cell edge size *vs.* Al content in sodalites synthesized in ethylene glycol (■) and in water using TMA^+ (*).[5] The expected expansion of the cell assuming no changes in T–O–T angles is plotted as a broken line.

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